

Narrative for a Lecture on Environmental Chemistry

Slide 1: Environmental chemistry is that branch of chemical science that deals with the production, transport, reactions, effects, and fates of chemical species in the water, air, terrestrial, and biological environment and the effects of human activities thereon.

ENVIRONMENTAL CHEMISTRY

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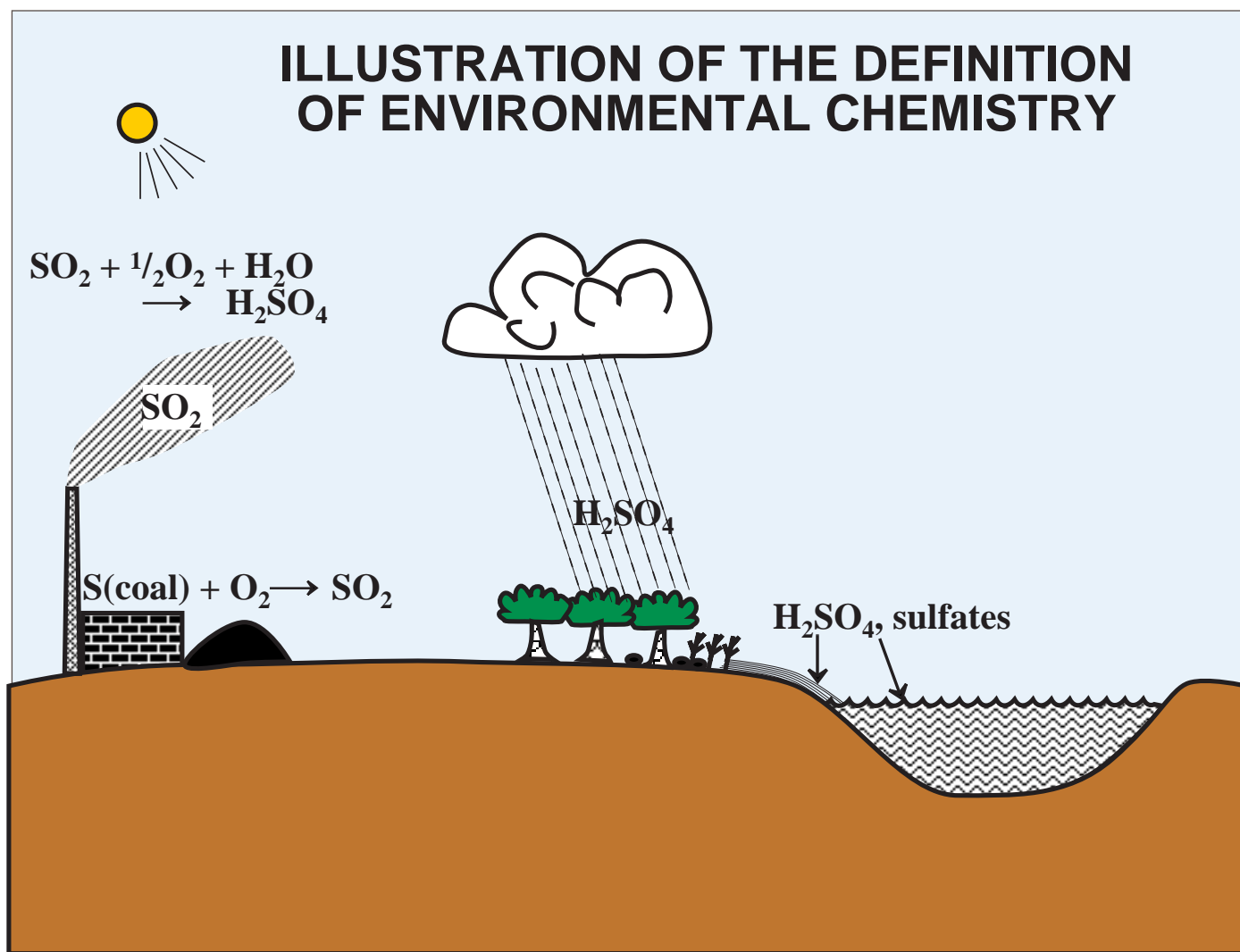
Reference: Stanley E. Manahan, *Fundamentals of Environmental Chemistry*, 3rd ed., Taylor & Francis/CRC Press, 2009 (manahans@missouri.edu)

For additional information about environmental chemistry and to download this and other presentations see:

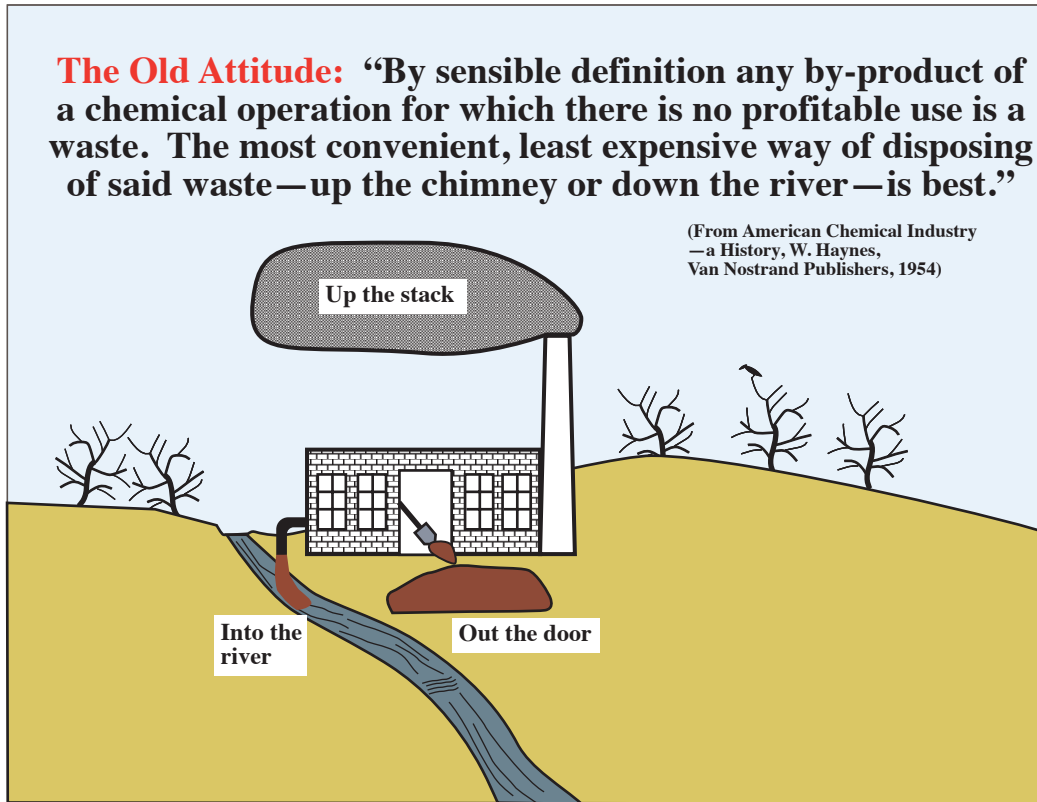
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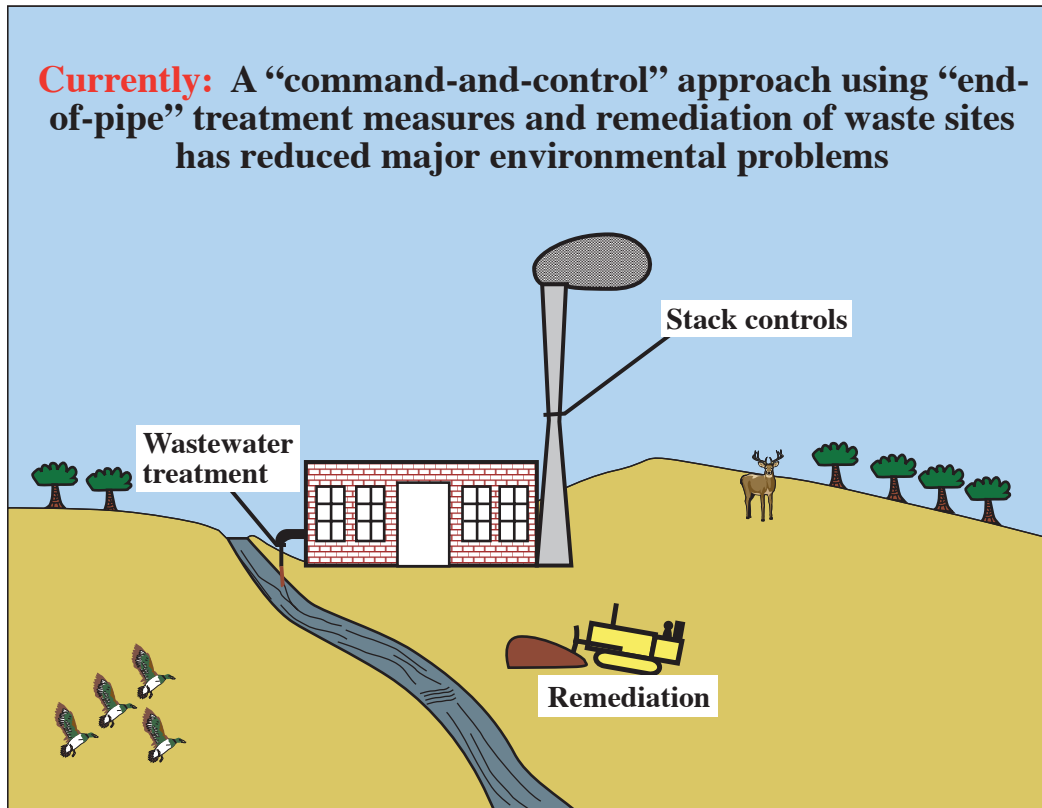
Slide 2: The definition of environmental chemistry is illustrated with a typical pollutant species. In this case sulfur in coal is oxidized to sulfur dioxide gas that is emitted to the atmosphere. The sulfur dioxide gas can be oxidized to sulfuric acid by atmospheric chemical processes, fall back to Earth as acid rain, affect a receptor such as plants, and end up in a "sink" such as a body of water or soil.



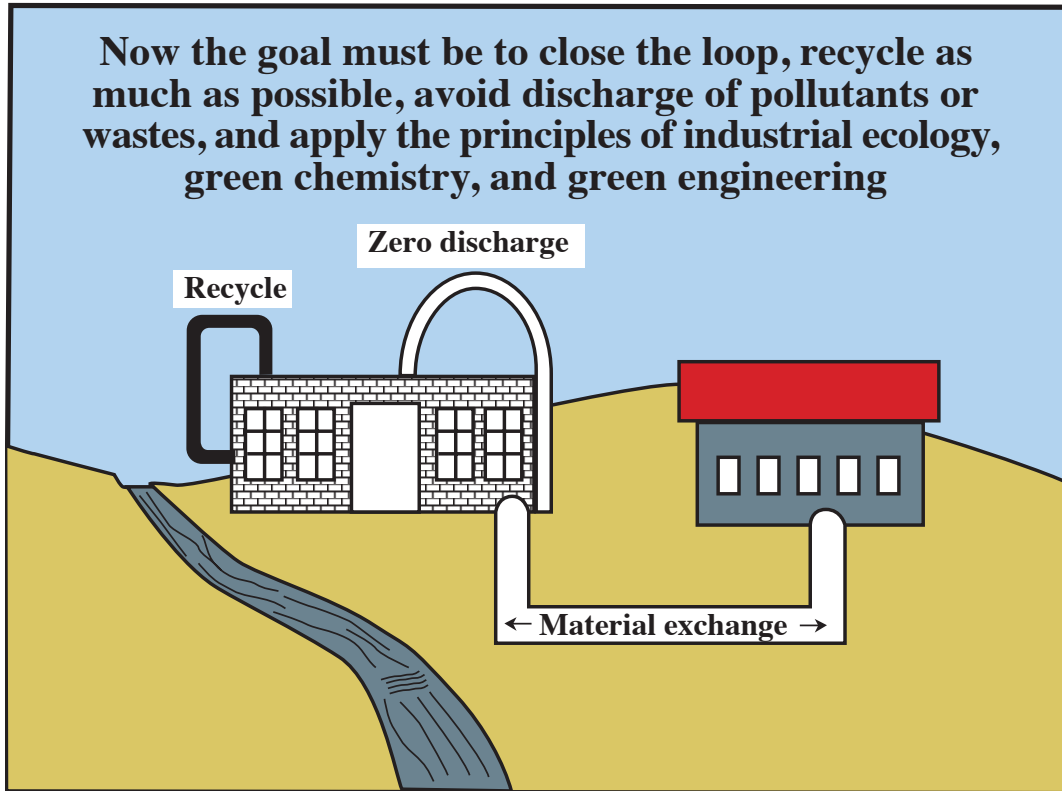
Slide 3: In the past many environmental problems were caused by practices that now seem to be totally unacceptable as expressed from the quote in this slide from what was regarded as a reputable book on the American chemical industry in 1954. The result was polluted air, polluted water, dangerous hazardous waste sites, and harm to living organisms.



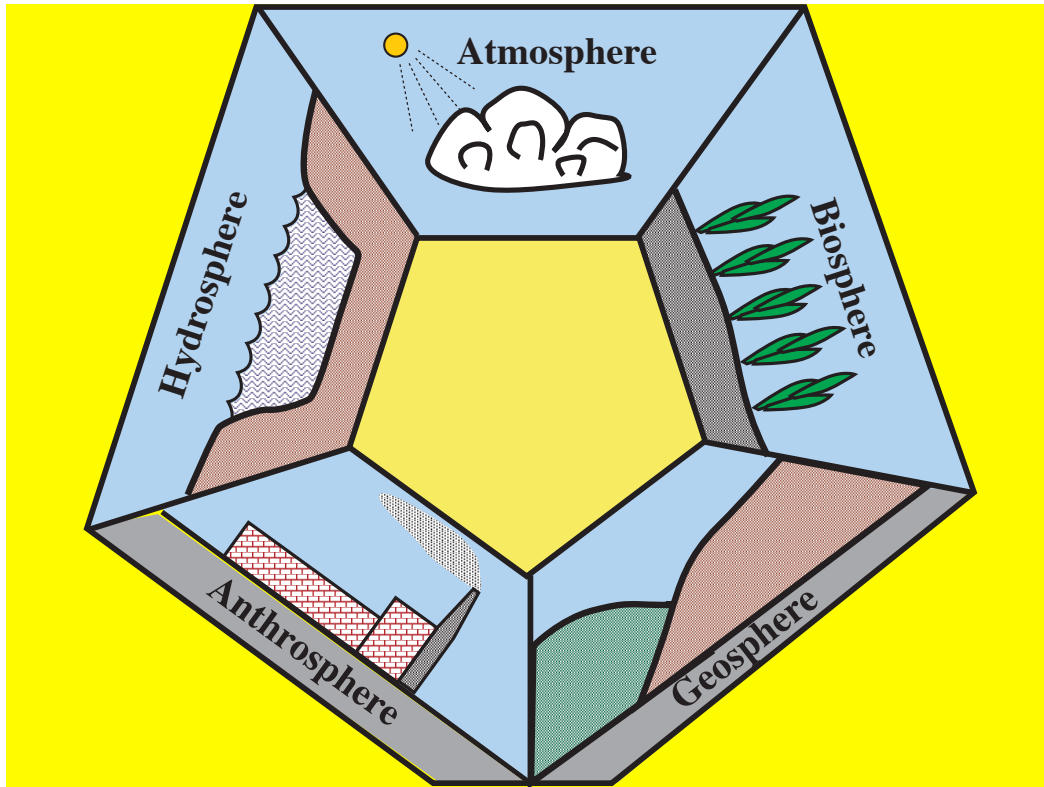
Slide 4: Dating from around 1970, laws and regulations were implemented to control air and water pollution and to clean up hazardous waste sites. These measures have relied largely upon “end of pipe” controls in which pollutants were generated but were removed before release to the environment. Although costly and requiring constant vigilance to make sure that standards have been met, these measures have been successful in reducing pollution and preventing increases in pollutant releases.



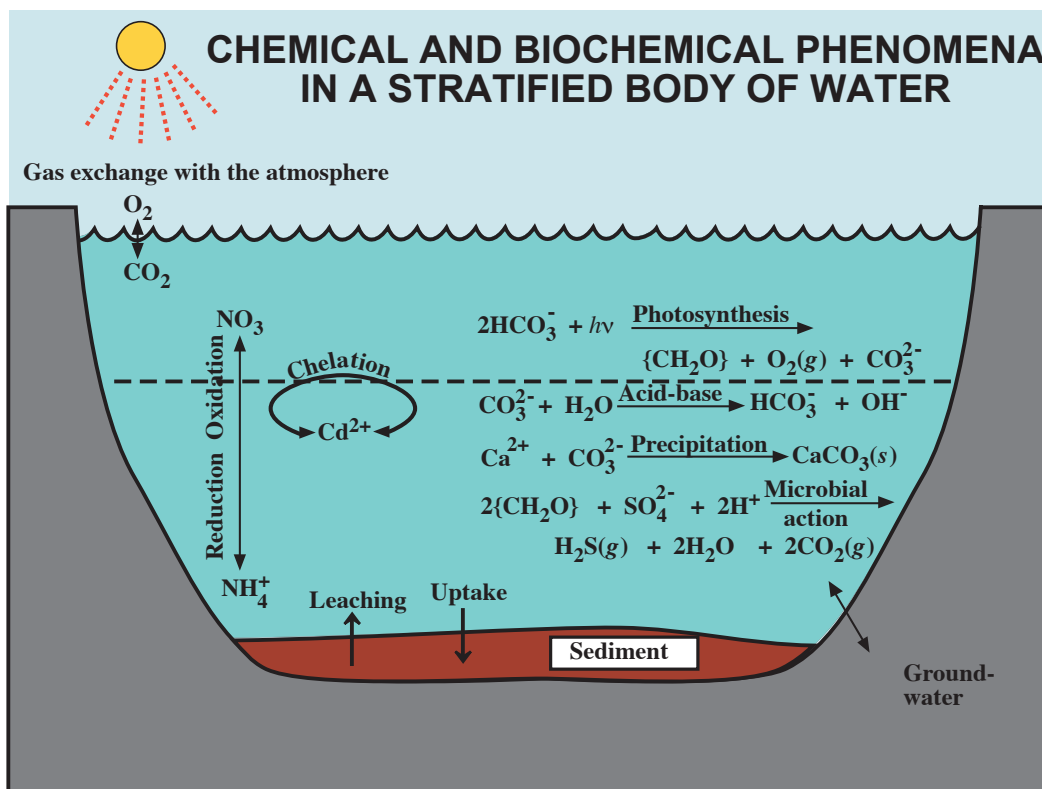
Slide 5: As an alternative to the regulatory approach, the tendency now is toward sustainability with systems that emphasize recycling of materials, exchange of materials between concerns, and zero discharge of wastes. Properly designed, such systems are inherently friendly to the environment and reduce the need for measures that emphasize purely pollution control.



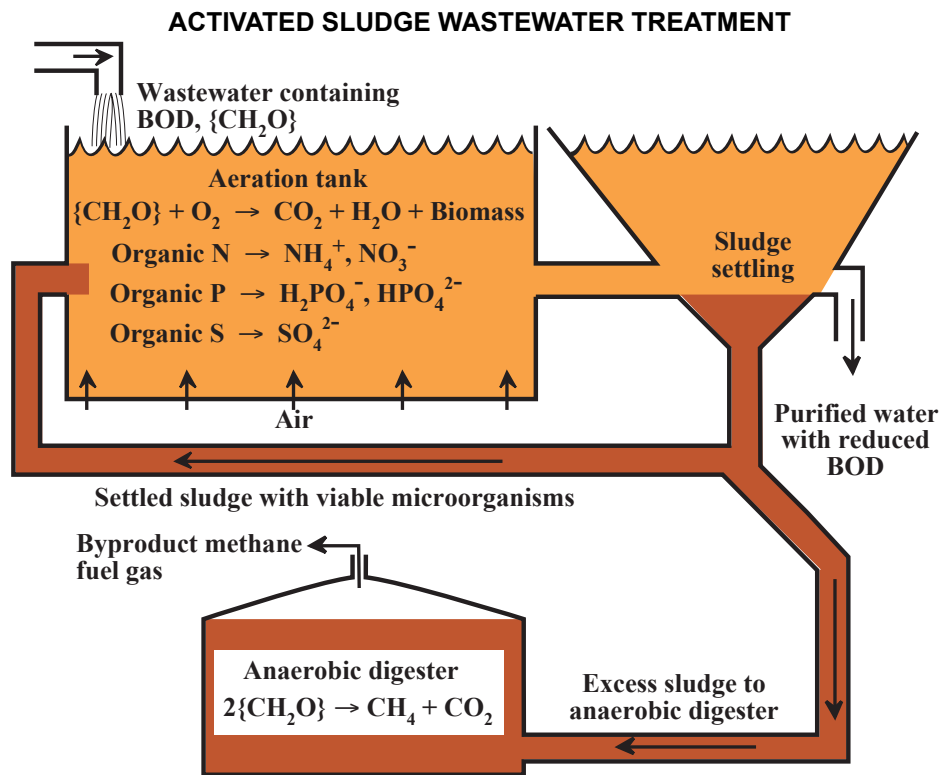
Slide 6: Traditionally, environmental science has considered four environmental spheres: water, air, living organisms, and earth. But it is important to consider a fifth environmental sphere, the anthrosphere, which consists of the things that humans make and do. The remainder of this lecture considers environmental chemistry within a framework of these five environmental spheres.



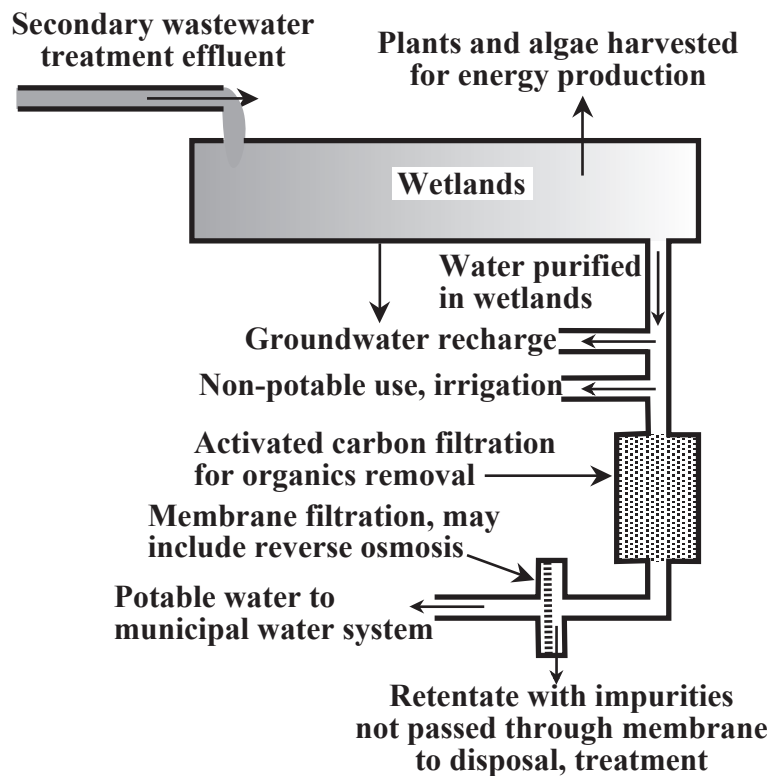
Slide 7: A variety of chemical and biochemical phenomena occur in the hydrosphere. Some of these are shown in this slide for a body of water stratified with a warmer oxygenated upper layer floating on top of a cooler oxygen-deficient lower layer, a common phenomenon during summer months. Gases are exchanged with the atmosphere at the surface and solutes are exchanged between water and sediment. Photosynthesis produces biomass, represented here as $[\text{CH}_2\text{O}]$. In the oxygen-deficient lower layer biomass undergoes biodegradation by the action of anoxic bacteria using oxidizing agents other than O_2 . When sulfate functions as the oxidizing agent odorous hydrogen sulfide gas may be evolved.



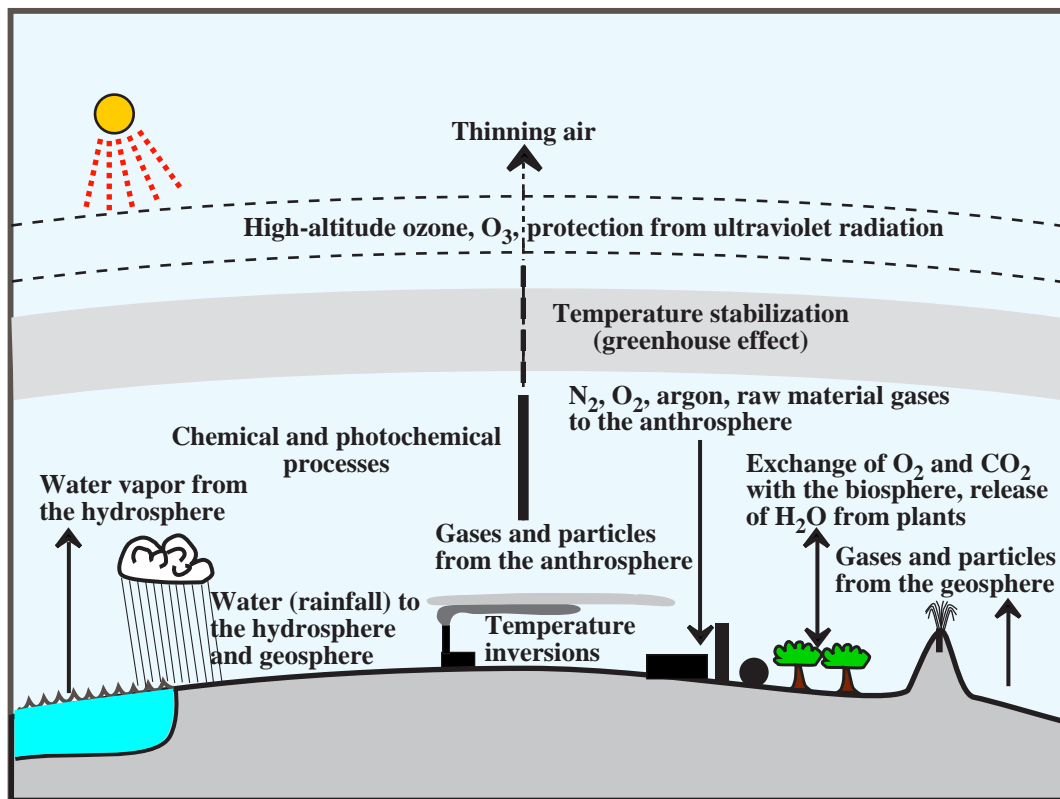
Slide 8: An important aspect of water chemistry is water treatment. This slide shows the activated sludge process used to treat municipal wastewater. A suspension of microorganisms in an aerated tank biodegrades organic wastes represented as $[CH_2O]$. This removes oxygen demand from the water so that it will not deplete oxygen when discharged to a stream or body of water. The microorganisms settle in a settling basin and are pumped back to the aeration tank, greatly speeding the biodegradation process. Excess microorganisms, sewage sludge or biosolids also represented as $\{CH_2O\}$, are taken to an anaerobic digester where they produce combustible methane, CH_4 , and carbon dioxide. The methane may provide fuel sufficient to run the engines that produce all the power needed by the plant.



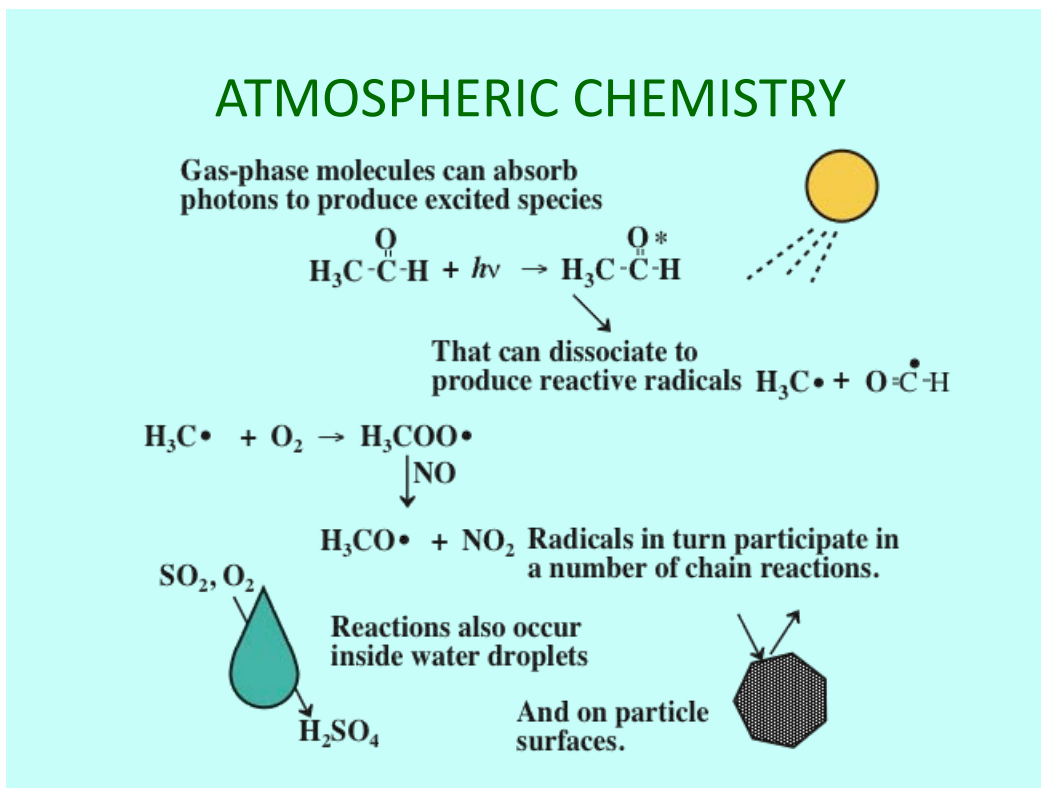
Slide 9: As water supplies become more limited around the world, renovation and re-use of wastewater become more important. This slide shows a system for purifying wastewater treated by the activated sludge process so that it can be used for applications such as groundwater recharge and irrigation. Advanced treatment processes can even bring the wastewater up to drinking water standards. A feature of the system shown is a wetlands area where algae and plants growing profusely in the fertile wastewater remove excess nutrients and produce biomass that can be converted to biofuels. The largest purification and water reuse project of its kind worldwide, the Orange County California Groundwater Replenishment System, utilizes a three-step process of microfiltration, reverse osmosis and ultraviolet light to purify highly-treated sewer water to state and federal drinking water standards (<http://www.gwrsystem.com/>).



Slide 10: The atmosphere is essential for life on Earth as a source of oxygen for organisms, carbon dioxide for plants, stabilization of surface temperatures (the good greenhouse effect), and protection from damaging ultraviolet radiation from ozone (O_3) in the stratosphere. Although the atmosphere extends far above Earth's surface, over 99% of it is within a few kilometers of the surface. In fact, if Earth were a classroom globe, virtually all of the atmosphere's air would be in a layer the thickness of the varnish on the globe! A distinctive feature of atmospheric chemistry is the ability of energetic photons of ultraviolet radiation (h ν) to put large amounts of energy into a single molecule as shown here for the photodissociation of stratospheric O_2 leading to ozone formation.



Slide 11: Atmospheric chemistry is complex involving literally hundreds of reactions. Photochemical reactions occur when photons of ultraviolet radiation split molecules apart producing reactive fragments with unpaired electrons (represented as dots in the slide) known as free radicals. These species undergo chain reactions such as those responsible for the ozone, organic oxidants, aldehydes, and solids characteristic of the unpleasant ingredients of photochemical smog that afflicts Los Angeles, Mexico City, and other urban areas around the world. Reactions such as the formation of sulfuric acid from sulfur dioxide may occur inside water droplets and on the surfaces of particles suspended in the atmosphere.



Slide 12: There are many different kinds of air pollutants. Particles obscure visibility and can be detrimental to respiration. Primary particles are those that enter the atmosphere as particles whereas secondary particles are produced by reactions of gases in the atmosphere. Several inorganic gases, mostly oxides of nitrogen, sulfur, and carbon are air pollutants. Photochemical smog results when nitrogen oxides and hydrocarbons in stagnant air masses subjected to solar radiation undergo photochemical reactions to form ozone, organic oxidants such as peroxyacetyl nitrate (PAN), aldehydes, and other species that tend to be detrimental to visibility, respiratory systems, and eyes.

AIR POLLUTANTS

Primary Particles

- Pollen
- Dust
- Fly ash
- Polycyclic aromatic hydrocarbons

Secondary Particles (formed from gas reactions)

- Smog particles
- Sulfuric acid droplets
- Salts such as $(\text{NH}_4)_2\text{SO}_4$

Inorganic Gases

- O_3
- SO_2
- NO
- NO_2
- CO
- H_2S
- HCl
- NH_3

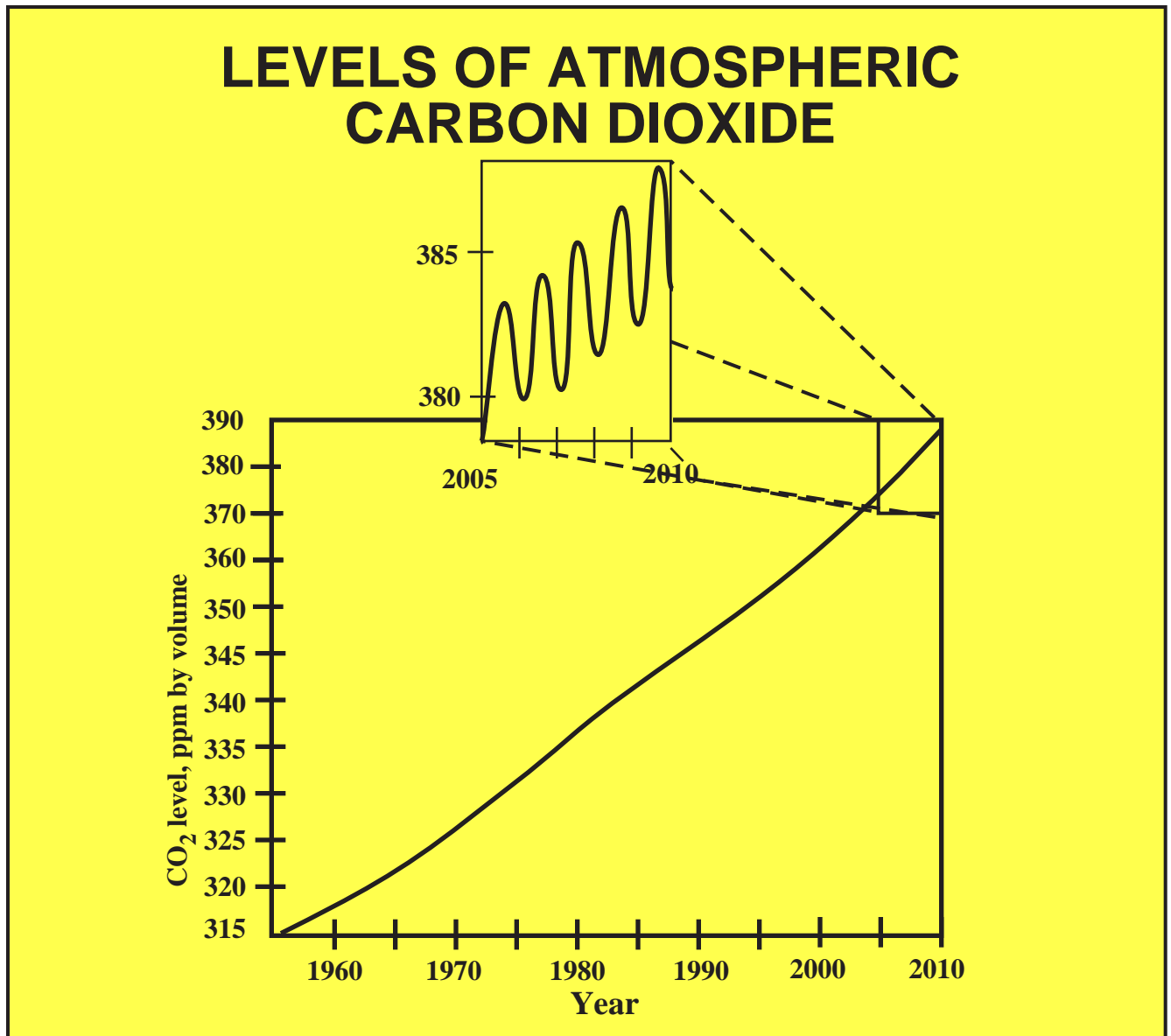
Organics

- Hydrocarbons including those that form photochemical smog
- Odorous organic sulfur compounds
- Organohalides
- Amines and other organonitrogen compounds
- Organo-oxygen compounds including aldehydes and ketones

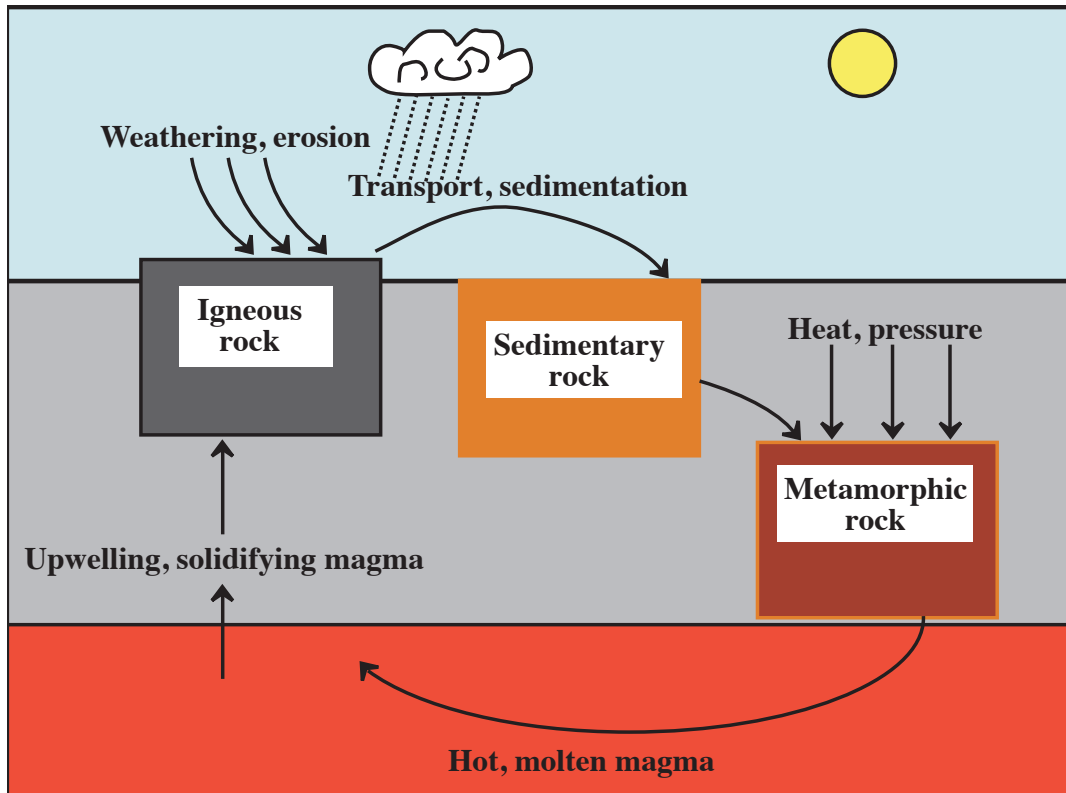
Photochemical Smog

- Smog particles
- Ozone
- Organic oxidants (PAN)
- Aldehydes

Slide 13: Although it is a normal constituent of the atmosphere essential to supply the carbon required for plant photosynthesis, carbon dioxide may turn out to be a harmful air pollutant at higher levels. This is because of its role in re-absorbing the infrared radiation by which Earth radiates back into space the solar energy received from the sun. This greenhouse effect is essential to life on Earth because it keeps the surface warm enough for living organisms to thrive. However, if too much carbon dioxide is present in the atmosphere, Earth's surface will become too warm the bad greenhouse effect leading to melting of polar ice caps and glaciers, elevated sea levels, severe droughts, and other detrimental effects. As shown in the plot, on this slide, atmospheric carbon dioxide levels from the burning of fossil fuels and other sources have been increasing by about 1 part per million per year, now closer to 2 parts per million per year. The resulting doubling of atmospheric carbon dioxide levels within the next century could have substantial, perhaps catastrophic, effects upon the global climate.



Slide 14: The geosphere has a very close relationship with the hydrosphere, the atmosphere, and the biosphere and is strongly affected by human activities in the anthrosphere. On Earth's surface, the geosphere is composed of rocks in turn made of various minerals and usually a thin layer of soil. Igneous rocks thrust upward by tectonic forces are broken down (weathered) by physical, chemical, and biological processes and material from them is deposited as sedimentary rock. Heat and pressure convert sedimentary rock to metamorphic rock. Heat and pressure convert sedimentary rock to metamorphic rock.



Slide 15: Geochemistry is the chemistry of rocks and minerals in the geosphere as it relates to the hydrosphere, atmosphere, biosphere, and, very recently in the geological timetable, the anthrosphere. The geochemical reaction shown in the slide is important in putting dissolved calcium and bicarbonate ion (water alkalinity) into water. The dissolution of calcium carbonate (limestone) by this process causes the formation of caves and cavities in limestone rock formations. Environmental geochemistry is the environmental branch of geochemistry and is important in considering the effects and fates of pollutants in the geosphere.

GEOCHEMISTRY

Geochemistry deals with chemical species, reactions, and processes in the geosphere and their interactions with the atmosphere and hydrosphere.

For example, carbon dioxide from the atmosphere dissolves in water in the hydrosphere, then reacts with limestone in the geosphere:



ENVIRONMENTAL GEOCHEMISTRY

Environmental geochemistry is the branch of geochemistry that explores the complex interactions among the rock/water/air/life systems that determine the chemical characteristics of the surface environment.

Slide 16: The geosphere is a crucial source of natural capital including essential metals, fuels, and plant nutrients. The geosphere is an important repository of wastes. One such waste for which the geosphere is likely to become a very important repository in the future is carbon dioxide from fossil fuel combustion that is currently released to the atmosphere where it causes global warming.

THE GEOSPHERE AS A SOURCE OF NATURAL CAPITAL

Natural capital is a term that describes the resources or value of the environment such as in providing essential materials or absorbing wastes

The geosphere is a crucial source of natural capital

- **Fuels, such as natural gas**
- **Metals, such as iron or copper**
- **Nonmetals, such as clay, sand, gravel**
- **Plant nutrients, such as phosphorus**
- **Absorption of wastes, such as carbon dioxide from fuel combustion pumped underground (carbon sequestration)**

The most important aspect of natural capital in the geosphere is the ability of soil to support plant growth for food production (next slide)

Slide 17: Soil is a crucial component of natural capital because all terrestrial organisms including humans depend upon it for their existence. The layer of productive soil on Earth's surface is extremely thin and subject to damage and erosion. Much productive soil has been lost or ruined and soil conservation is a top priority for sustainability.

SOIL: THE MOST IMPORTANT GEOSPHERIC RESOURCE

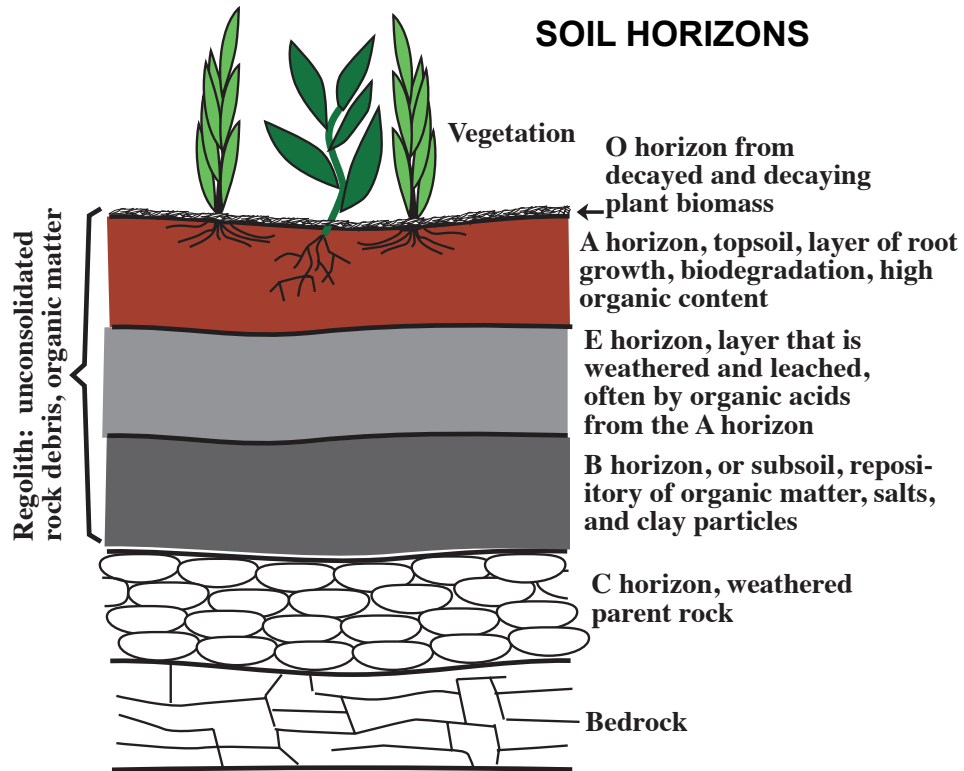
Soil is obviously of crucial importance as a support for plant growth

Soil is composed of finely divided, highly weathered mineral matter and organic matter from the partial biodegradation of plant material

Earth's soil is a very thin layer; if Earth were a classroom globe, the average thickness of the total soil resource would be about the same as the diameter of a human cell!

Soil is divided into layers called soil horizons (next slide)

Slide 18: Soil is typically divided into layers called horizons. Many important chemical and biochemical reactions occur in soil. Soil is subject to water and wind erosion, and one of the earliest environmental movements, dating back to around 1900 in the U.S., has been soil conservation. Large areas of formerly productive agricultural land have been turned to desert by poor agricultural and animal grazing practices, a large problem for sustainability.

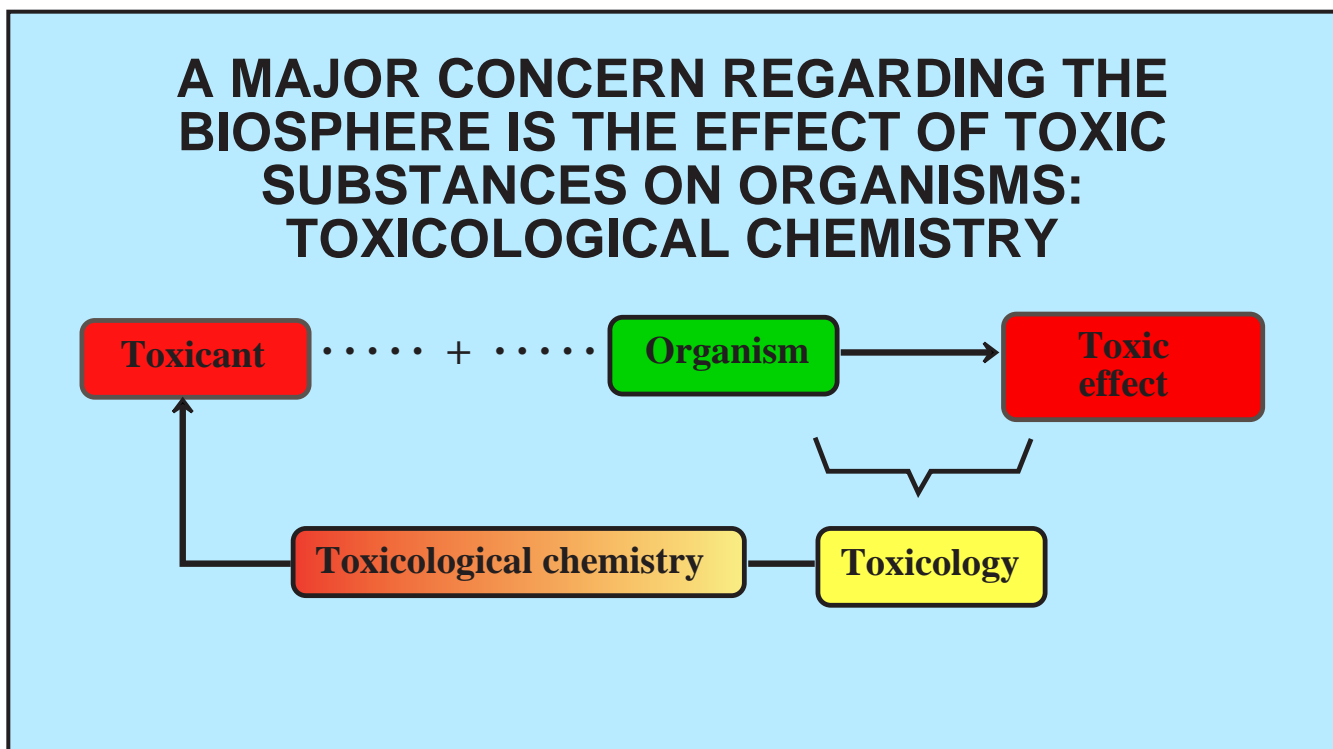


Slide 19: Living organisms constitute the biosphere. Through photosynthesis of plants and algae it is the basis of the food chain. In addition to food, the biosphere is a crucial source of biomass for raw material and, in the future, for synthetic fuel. This slide shows a heavy growth of switchgrass, a plant that is remarkably productive of biomass on poor soil and that has significant potential as a renewable fuel resource.

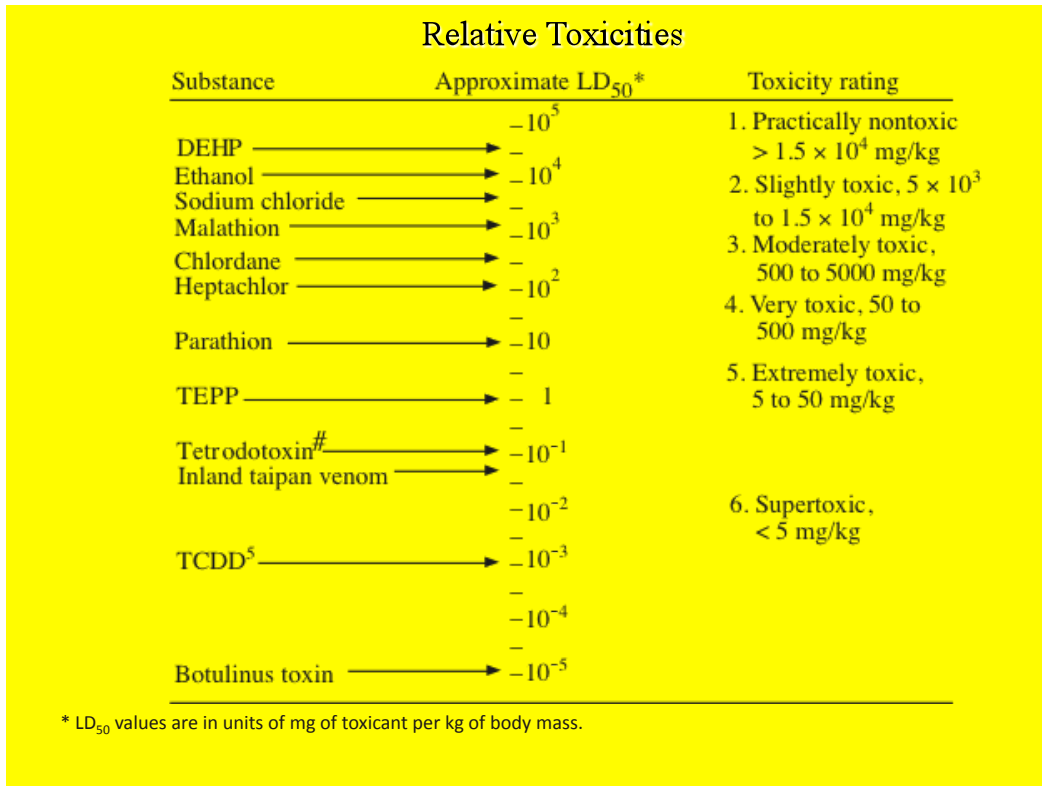
THE BIOSPHERE
SWITCHGRASS, A POTENTIALLY IMPORTANT
SOURCE OF BIOMASS

**A photograph of a heavy growth of switchgrass is shown here
in the PowerPoint presentation**

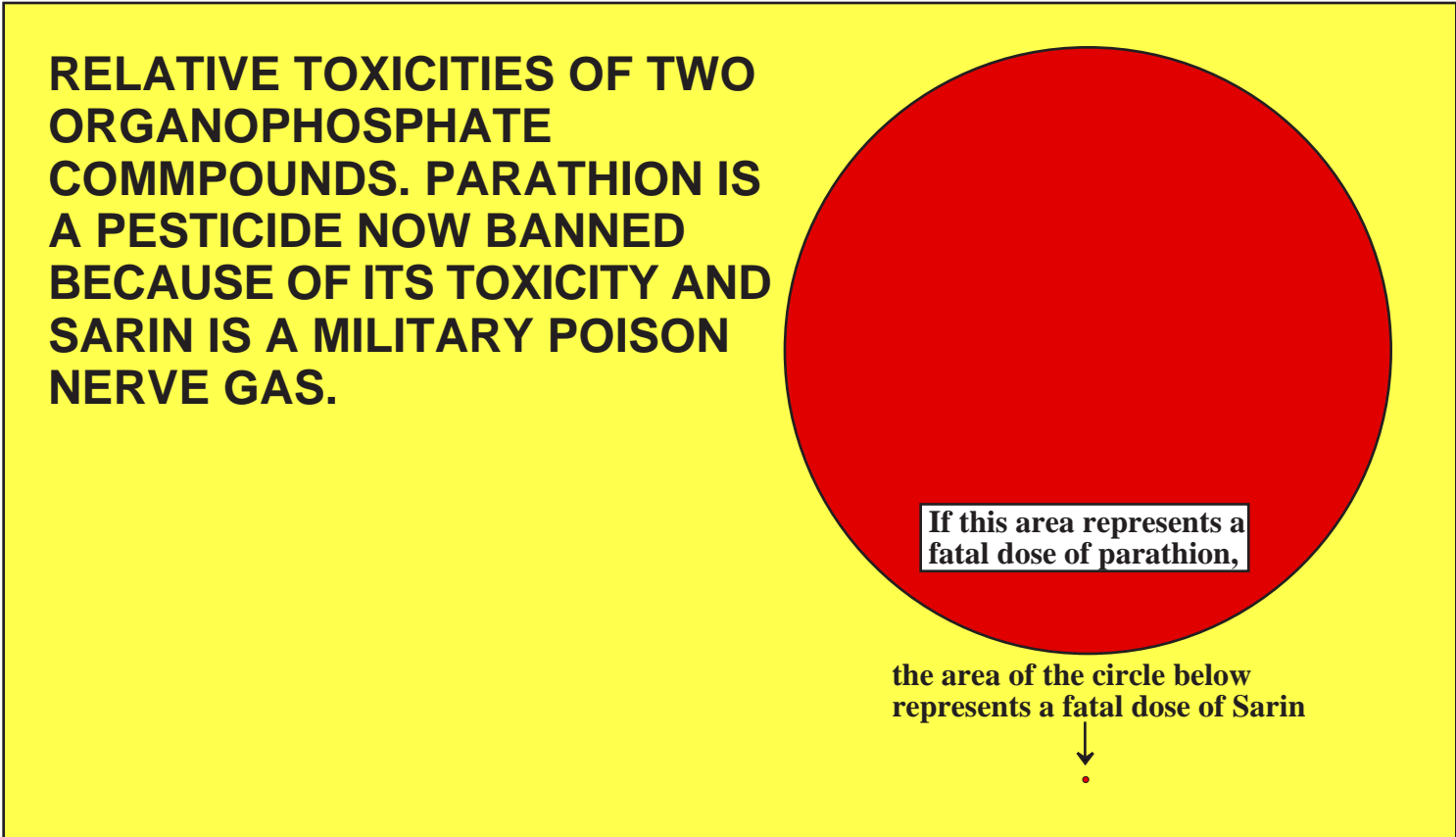
Slide 20: A major consideration with respect to the biosphere is the effect of toxic substances on organisms. Toxicological chemistry addresses the relationship between the chemical nature of substances and their toxic effects.



Slide 21: An interesting aspect of toxicological chemistry is the wide range of toxicities of various substances. The LD₅₀ values shown in this slide are the doses in mg toxic substance to kg body mass estimated to kill 50% of test subjects. Diethylhexylphthalate (DEHP) is a low toxicity plasticizer added to plastics such as polyvinylchloride to make them more flexible. Malathion, an organophosphate insecticide, is relatively safe because mammals, but not insects, can hydrolyze the molecule to safe materials. Though an effective, highly biodegradable organophosphate insecticide, parathion is now banned because of its toxic effects. Tetrodotoxin is the toxin of the puffer fish. The Australian inland taipan snake is known as a “two-step” snake; if it strikes you, you take two steps then fall down dead. TCDD is the infamous dioxin, which causes an unsightly chloracne skin condition in humans but is deadly to some other species such as guinea pigs. Botulinus toxin produced by botulinus bacteria is one of the most toxic substances known, but in dilute form has many medical uses and is the basis of Botox used to remove skin wrinkles.

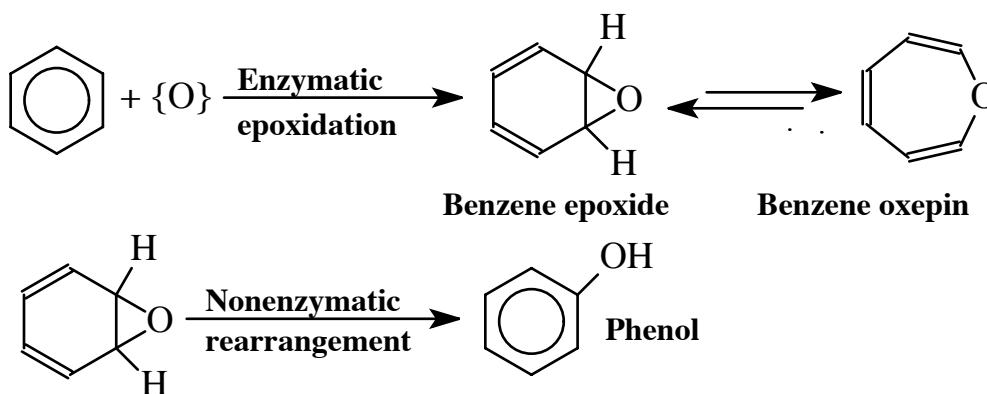


Slide 22: Illustrating the great differences in toxicities of substances, if the big red circle represents a fatal dose of parathion organophosphate insecticide, now banned because of its toxicity if not handled properly, the little black dot represents a fatal dose of organophosphate Sarin nerve gasóquite a difference!

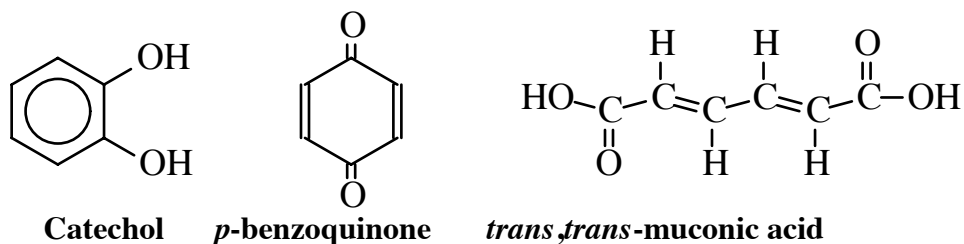


Slide 23: The body metabolizes toxic substances to detoxify them. Benzene, once widely used as a solvent and reagent in organic chemistry laboratories, but now discontinued because of its potential to cause blood abnormalities and possibly leukemia, is metabolized by cytochrome P-450 enzymes to products such as phenol and *trans,trans*-muconic acid that are eliminated through urine. Benzene oxepin and benzene oxide are reactive intermediates that react with biomolecules in the body to produce the toxic effects of benzene.

EXAMPLE OF BENZENE METABOLISM THAT CAUSES BLOOD ABNORMALITIES

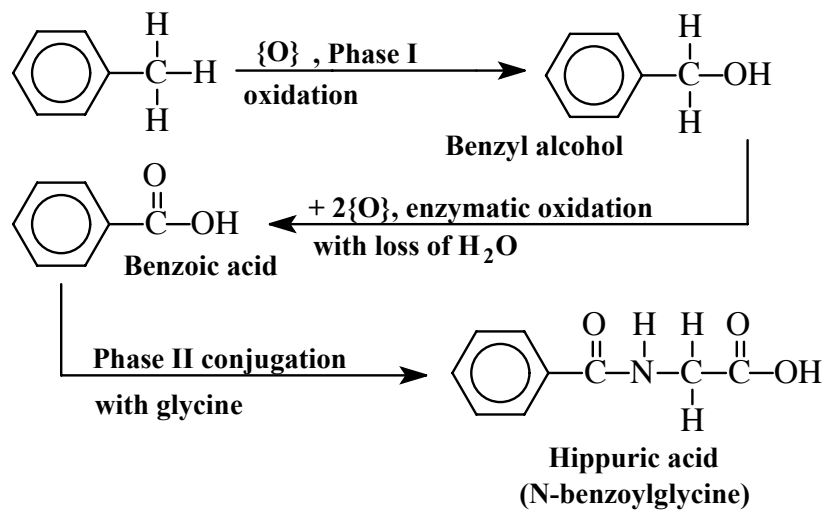


Other metabolic products including the following:

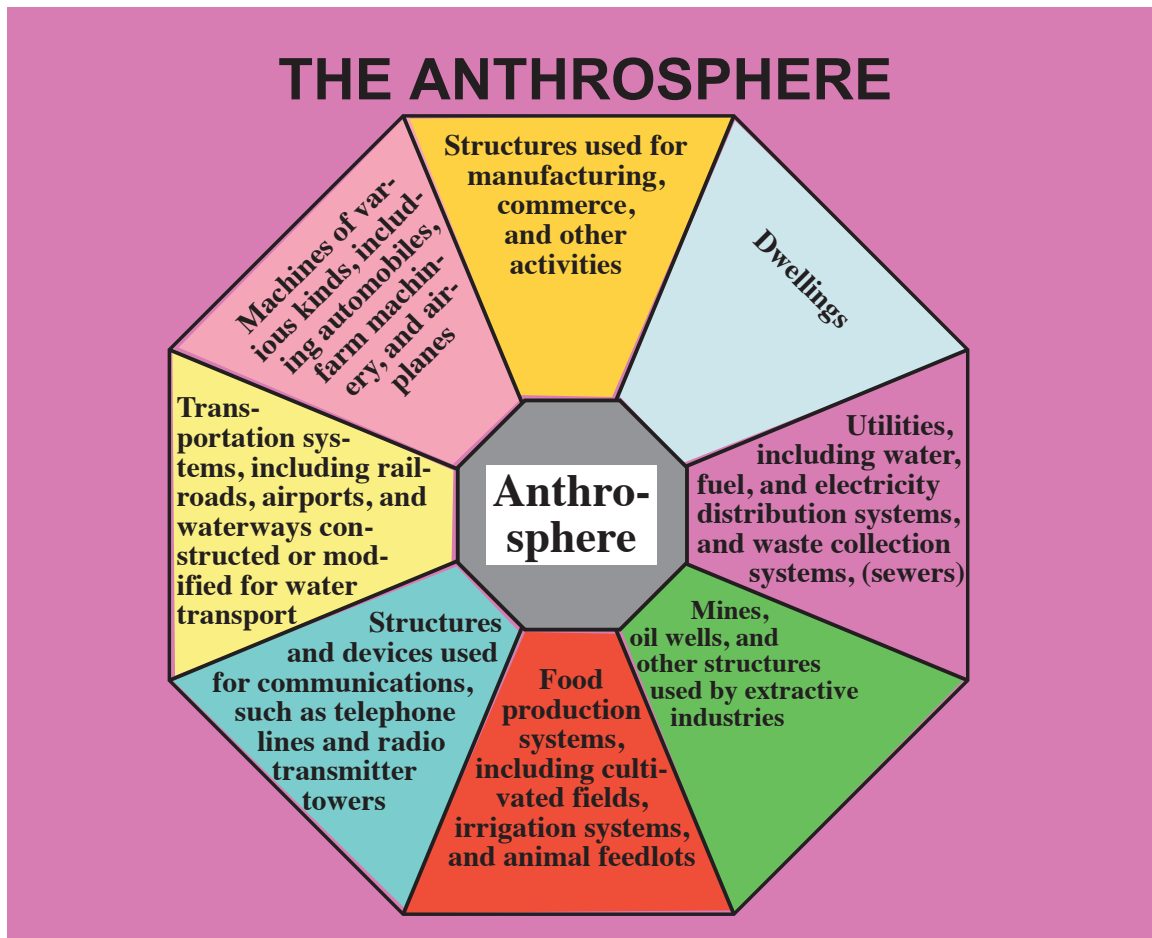


Slide 24: Benzene has been replaced in the laboratory with toluene, which has solvent and chemical properties that are largely similar to those of benzene. However, the $-CH_3$ side group on toluene is readily oxidized by body enzymes to benzoic acid, a harmless, common food metabolite. Benzoic acid is conjugated with one of the body's natural amino acids, glycine, to produce hippuric acid, which is eliminated through urine. Some older organic chemistry laboratory manuals recommend collecting urine from horses from which hippuric acid can be extracted. The collection procedure is at best messy and can be hazardous because horses are notorious for objecting to donation of their body fluids or parts to science.

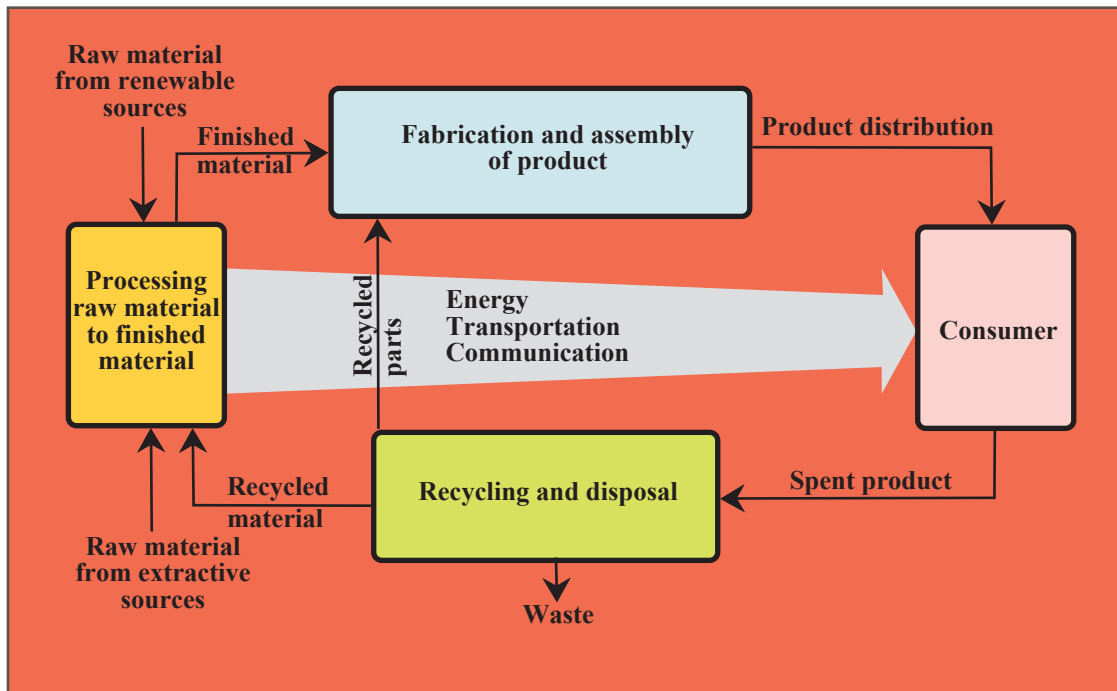
BENZENE IS LARGELY REPLACED BY TOLUENE, WHICH IS METABOLIZED TO HARMLESS PRODUCTS



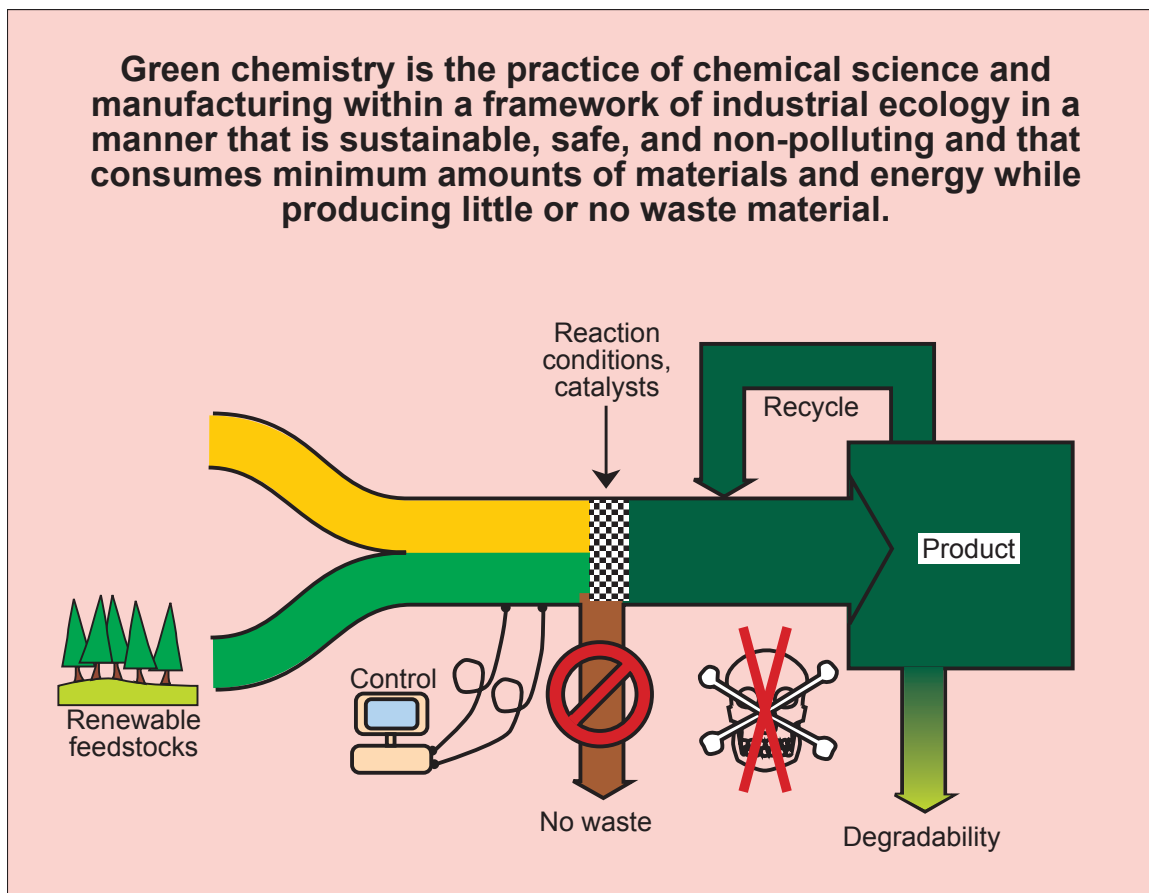
Slide 25: The anthrosphere is the fifth environmental sphere to be considered. It consists of the many things that humans make or do, only a few of which are shown here. The anthrosphere is so important in determining conditions on Earth that in 2000 the Nobel Prize winning atmospheric scientist Paul Crutzen made a convincing argument that we are now leaving the Holocene Epoch, which began with the latest interglacial period about 12,000 years ago and have entered the Anthropocene Epoch in which human activities, such as emissions of massive amounts of global-warming carbon dioxide to the atmosphere, predominate in determining Earth's environment.



Slide 26: Shown here is a general outline of a manufacturing process in the anthrosphere such as might be used in the chemical industry. One aspect of manufacturing that has caused many problems is the production and improper disposal of hazardous waste substances including toxic heavy metals and organochlorine compounds that have a tendency to undergo bioaccumulation. One of the most notorious hazardous waste disposal sites in the U.S. is the Love Canal site near Niagara Falls, New York, where 21,000 tons of chemical wastes containing more than 80 different compounds were disposed.



Slide 27: Dating from the 1990s, green chemistry has become an important discipline in the practice of sustainable, environmentally safe chemical science and technology.

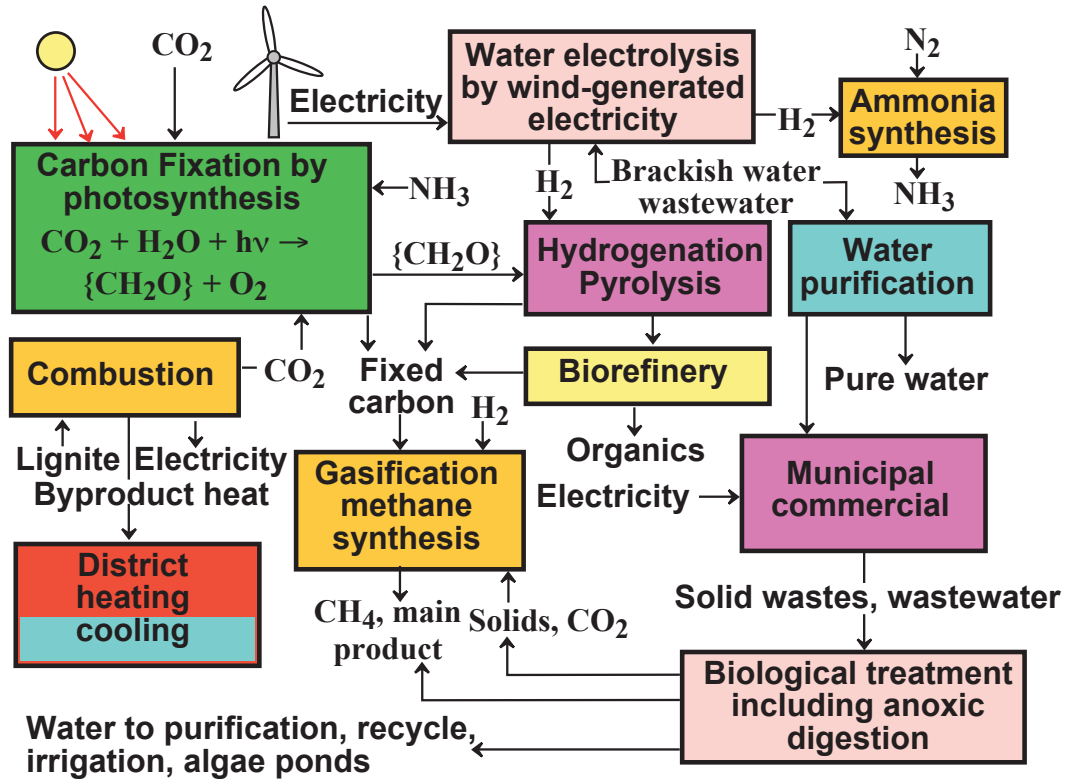


Slide 28: Industrial ecology dating from around 1990 is very much related to green chemistry. It calls for various enterprises to practice industrial metabolism co-existing to mutual advantage in industrial ecosystems.

INDUSTRIAL ECOLOGY

Industrial ecology views an industrial system as an artificial ecosystem, with primary sources of raw materials and energy and with a number of enterprises making use of what would otherwise be waste products of other members of the system practiced in a manner that minimizes environmental impact while optimizing utilization of resources, energy, and capital.

Slide 29: A number of industrial ecosystems have developed around the world, the most commonly cited example of which is the one in Kalundborg, Denmark. Here is shown a hypothetical industrial ecosystem in which methane (natural gas) is produced thermochemically from carbon fixed as organic matter, represented as $\{CH_2O\}$ using as a reagent elemental hydrogen produced from the electrolysis of water by windpower.



Slide 30: Sustainability must be the goal, leaving Earth in a condition to support future generations with a good quality of life.

**It is All About Sustainability: Leaving Earth
in a Condition to Support Future
Generations**

Slide 31: When it comes to sustainability, energy is the key component. For a sustainable world future energy supplies must be sustainable, abundant, safe, environmentally benign, and affordable. Meeting these criteria is a huge challenge.

ENERGY: KEY TO SUSTAINABILITY

Sustainability requires energy that is

- **Sustainable**
- **Abundant**
- **Safe**
- **Essentially harmless to the environment**
- **Affordable**

Slide 32: Abundant, sustainable energy can enable accomplishment of all of the goals listed in this slide plus many more.

ENERGY SOURCES MEETING THESE CRITERIA CAN

- **Provide electricity**
- **Provide comfort for dwellings even in harsh environments**
- **Meet transportation needs**
- **Desalinate seawater to provide abundant water supplies**
- **Renovate wastewater to drinking water standards**
- **Enable soil restoration**
- **Synthesize abundant nitrogen fertilizer for crops**
- **Destroy hazardous wastes or put them into a nonhazardous form**
- **Eliminate air and water pollutants**

Slide 33: There are many energy alternatives, a number of which are from renewable sources.

THE MAJOR ENERGY ALTERNATIVES

- Fossil fuels
 - Petroleum (running out, CO₂ emissions)
 - Natural gas (minimal CO₂ emissions, in short supply during recent years, supplies have started increasing from unconventional sources such as tight shales)
 - Coal (abundant, high CO₂ emissions)
- Nuclear
- Hydro
- Solar
- Wind
- Tidal
- Wave
- Geothermal
- Biomass

Slide 34: Arguably the most promising renewable energy alternative is windpower. One problem with it is its intermittent nature, although some places such as parts of the Texas panhandle have essentially constant wind. Windpower can be used to generate elemental hydrogen used as a fuel and chemical reagent for synthetic fuels production which overcomes any problems from its intermittent nature.

WIND ENERGY

- Fastest growing energy technology in the world
- Enough wind energy resources on- and offshore to more than meet the electrical energy needs of the country
- Intermittent
- As of 2009, 25,300 mw capacity of windpower in the U.S. led by Texas

A photograph of a windmill in the Netherlands is shown here in the PowerPoint presentation

Slide 35: Earth is the only home we have and ever can have. Environmental chemistry and the practice of green chemistry and related areas such as industrial ecology are essential to sustaining our home.

**EARTH IS THE ONLY HOME WE HAVE AND EVER CAN HAVE
ENVIRONMENTAL CHEMISTRY IS ESSENTIAL TO SUSTAINING OUR HOME**

A photograph of Earth as viewed from space is shown here in the PowerPoint presentation